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Atmospheric 14CO2 Constraints on and Modeling of Net Carbon Fluxes 06-ERD-031 An LLNL Exploratory Research in the Directorate's Final Report

T. P. Guilderson, P. Cameron-Smith, D. Bergmann, H. D. Graven, R. Keeling, K. Boering, K. Caldeira

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Atmospheric $^{14}CO_2$ Constraints on and Modeling of Net Carbon Fluxes
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Thomas P. Guilderson
Center for Accelerator Mass Spectrometry

Philip Cameron-Smith, Dan Bergmann
Earth Systems & Atmospheric Sciences Division

Heather D. Graven, Ralph Keeling
Scripps Institution of Oceanography, University of California - San Diego

Kristie Boering
Dept. of Chemistry, University of California - Berkeley

Ken Caldeira
Dept. of Global Ecology, Carnegie Institution – Stanford California

Abstract

A critical scientific question is: "what are the present day sources and sinks of carbon dioxide (CO_2) in the natural environment, and how will these sinks evolve under rising CO_2 concentrations and expected climate change and ecosystem response?" Sources and sinks of carbon dioxide impart their signature on the distribution, concentration, and isotopic composition of CO_2. Spatial and temporal trends (variability) provide information on the net surface (atmosphere to ocean, atmosphere to terrestrial biosphere) fluxes. The need to establish more reliable estimates of sources and sinks of CO_2 has lead to an expansion of CO_2 measurement programs over the past decade and the development of new methodologies for tracing carbon flows. These methodologies include high-precison pCO_2, $\delta^{13}CO_2$, and $[O_2/N_2]$ measurements on atmospheric constituents that, when combined, have allowed estimates of the net terrestrial and oceanic fluxes at decadal timescales. Major gaps in our understanding remain however, and resulting flux estimates have large errors and are comparatively unconstrained.

One potentially powerful approach to tracking carbon flows is based on observations of the $^{14}C/^{12}C$ ratio of atmospheric CO_2. This ratio can be used to explicitly distinguish fossil-fuel CO_2 from other sources of CO_2 and also provide constraints on the mass and turnover times of carbon in land ecosystems and on exchange rates of CO_2 between air and sea. Here we demonstrated measurement of $^{14}C/^{12}C$ ratios at 1-2‰ on archived and currently collected air samples. In parallel we utilized the LLNL-IMPACT global atmospheric chemistry transport model and the TransCom inversion algorithm to utilize these data in inversion estimates of carbon fluxes. This project has laid the foundation for a more expanded effort in the future, involving collaborations with other air-sampling programs and modeling groups.

General Background

Carbon dioxide (CO_2) is the most important man-made greenhouse gas influencing global climate. The atmospheric concentration of CO_2 has risen from ~280ppm in the early 1800s to ~385ppm today primarily from the utilization of fossil fuels, cement production, and land use practices. Paleo-atmospheric measurements on air bubbles trapped in ice cores document that present values are the highest that they have been in at least the last 740000 years and the rate of change is unprecedented, even on glacial-interglacial time scales. Carbon dioxide concentrations are currently rising at ~1.5 ppm/yr, a rate which is controlled not just by the emissions from biomass and fossil-fuel burning, but also by the variable exchanges of CO_2 with the oceans and land biota. Less than half of the estimated ~280 petagrams (Gt) of fossil-fuel carbon and ~190 Gt of land-use carbon reside in the atmosphere; the remaining anthropogenic carbon has been partitioned into the terrestrial biosphere and oceans. Uptake by the terrestrial biosphere is a consequence of excess primary production relative to respiration and decomposition and is portioned into fast (decades) and slow (millennia) carbon pools. Ocean uptake is accomplished by physical (air-sea) processes and is governed by carbonate chemistry, ocean dynamics, and biological productivity. Carbon sequestration in the ocean has a residence time in keeping with the residence time of the respective water masses. The deep interior ocean residence time is centuries to millennia and that of the shallow circulation on the order of decades. Upwelling significantly influences the interannual ocean CO_2 flux. Time series of precisely measured atmospheric constituents are critical to understand the fate and transport of (anthropogenic) carbon in the contemporary carbon cycle. Due to the pioneering work of C. Keeling, atmospheric CO_2 concentrations have been continuously measured at Mauna Loa and the South Pole since 1957. These initial stations have grown into a loosely confederated network of surface stations with quasi-global coverage. The stable carbon isotope (^{13}C:^{12}C) ratio ($\delta^{13}C$) of atmospheric CO_2 on flask samples was added in the late 1970s. The $\delta^{13}C$ of atmospheric CO_2 can be used to estimate the partitioning of carbon uptake between the terrestrial biosphere and ocean. The rationale relies on fractionation during photosynthesis, where the $\delta^{13}C$ of plants that follow the C3 photosynthetic pathway are 1.8% more negative relative to atmospheric CO_2. Air-sea exchange of CO_2 involves only a minor fraction effect. The combustion of fossil fuel results in an overall decrease in $\delta^{13}C$ since fossil fuel carbon $\delta^{13}C$ is more negative than atmospheric CO_2. [CO_2] and $\delta^{13}CO_2$ measurements with a prescribed turnover in the terrestrial biosphere and ocean can result in one unconstrained solution of the partitioning of the net carbon fluxes.

Measurements of the concentration of atmospheric oxygen [O_2], which began in the early 1990s, can provide complementary information to [CO_2] and $\delta^{13}CO_2$. The concentration of oxygen in the atmosphere reflects the net biosphere production (photosynthesis – respiration) balanced by that consumed by fossil fuel combustion. CO_2 uptake by the ocean has no direct effect on atmospheric [O_2] whereas terrestrial uptake yields a net flux to the atmosphere. It is assumed that the oceanic biosphere remains nutrient limited with no net effect on atmospheric [O_2] trends.

Seasonal to interannual variability of the respective net fluxes is much larger than

the uncertainty in the decadal averages which has made it difficult to quantify sinks and sources on shorter annual timescales. Complications to $\delta^{13}C$, $[O_2]$, and $[CO_2]$ based carbon flux estimates exist. First, in addition to C3 plants there are C4 and CAM plants that discriminate much less against ^{13}C than C3 plants (*ie.*, $\delta^{13}C$ is more positive), thus for meaningful analysis the relative distribution of C3 and C4 plants must be known. Second, although the oceanic disequilibrium value is close to zero it changes with changing atmospheric $\delta^{13}CO_2$. Common to both $[O_2]$ and $\delta^{13}C$ methods is a requirement that the oceanic and terrestrial carbon residence times be provided. Finally, there is an implicit assumption that the fossil fuel fluxes are well known. Briefly touched upon earlier was the fact that the net fluxes to/from the ocean / terrestrial biosphere are two uni-directional fluxes (*e.g.* Fnetatmbio = Fatmbio + Fbioatm). If we were to construct a system of linear equations we would find that an accurate and precise solution is underconstrained. An additional carbon tracer would allow for more accurate estimates of the net fluxes.

Radiocarbon ($t_{1/2}$ 5730yrs), is produced naturally in the stratosphere by the collision between cosmic-ray generated secondary neutrons and ^{14}N. Upon formation ^{14}C is rapidly oxidized to CO_2 and exchanges with the terrestrial biosphere and oceans. In the mid 1950s to early 1960s the ^{14}C content in the atmosphere doubled from its $^{14}C/^{12}C$ ratio of $1.18x10^{-12}$. Since 1963, the $^{14}C/^{12}C$ ratio, (normally reported as $\Delta^{14}C$ which includes a correction for mass dependent fractionation), has decreased. Atmospheric $\Delta^{14}C$ reflects variations in fossil fuel emissions (^{14}C-free), ocean-atmosphere exchange, stratosphere-troposphere mixing, and terrestrial ecosystem fluxes. As a consequence of the redistribution of "anthropogenic"-^{14}C into and with the terrestrial and ocean reservoirs, the spatio-temporal variability of $^{14}CO_2$ has decreased. In the mid 1960s across the mid to high latitudes of the northern hemisphere the seasonal cycle of $\Delta^{14}C$ was in excess of 50‰ with similar phasing of the seasonal cycle; maximum values were reached in the boreal summer and a minimum in winter. This seasonality was driven by a combination of seasonal (spring-summer) troposphere-stratosphere exchange and the increased use of fossil fuel during winter. In more recent decades, the seasonal amplitude has generally decreased, although regions with larger fossil fuel emissions tend to have a larger peak to trough amplitude than "clean-air" locations.

Radiocarbon as a Carbon Cycle Tracer

(i) Constrain fossil-fuel emissions. $\Delta^{14}C$ is probably the best available tracer for resolving fossil-fuel CO_2 from other sources of CO_2. While other tracers, like O_2/N_2 and $^{13}C/^{12}C$, are useful for distinguishing land versus oceanic components of the CO_2 variations, these tracers do not, in fact, distinguish between land biospheric and fossil-fuel components. Neither do current inverse model calculations. To separate land exchanges into fossil-fuel and land biospheric components, using inverse techniques or using O_2/N_2 or $^{13}C/^{12}C$ data, it is necessary to apply corrections for the effects from fossil-fuel. Typically these corrections are based on statistical compilations for the distribution of fossil-fuel burning in combination with atmospheric transport models. Both of these have sizeable uncertainties, especially at smaller space (regional) and time (seasonal) scales. Model simulations indicate that fossil-fuel burning should produce $\Delta^{14}C$ deficits of 15 to 25‰ over N. America and Eurasia. By helping to resolve the fossil-fuel

contribution to CO_2 variability $\Delta^{14}C$ measurements could play a direct role in improving estimates from inversion calculations of the land biospheric flux over North America. Measurements would also provide independent constraints on rates of fossil-fuel burning.

(ii) Constrain rates of ocean ventilation and mixing. While atmospheric $\Delta^{14}C$ is not sensitive to the net uptake of anthropogenic CO_2 by the oceans, it is sensitive to the gross (*i.e*. two-way) exchanges that swap ^{14}C atoms with ^{12}C atoms across the air-sea interface. These exchanges tend to lower atmospheric $\Delta^{14}C$ since the ocean is a large reservoir of ^{14}C deficient carbon. The effectiveness of this exchange depends both on rates at which CO_2 molecules are exchanged across the air-sea interface as well as on rates of internal ocean mixing. These gross air-sea exchanges are a major driver of the long-term decrease in atmospheric $\Delta^{14}C$ in recent decades. The exchanges also can contribute to the $\Delta^{14}C$ gradients within the atmosphere. Measurements at background stations by the Heidelberg group show that the lowest $\Delta^{14}C$ values are found, not over the Northern Continents, as expected from fossil-fuel burning, but rather over the Southern Ocean, where the high rates of vertical mixing and air-sea exchange cause a regional reduction in $\Delta^{14}C$ in the overlying air. The magnitude of this regional deficit is sensitive to rates of gas exchange and ocean mixing. The measurements can thus contribute to helping to characterize these processes and their stability over time. These same processes also control the rate at which anthropogenic CO_2 is taken up by the ocean, so atmospheric $\Delta^{14}C$ measurements, especially when combined with measurements of $\Delta^{14}C$ in the water, can contribute to improved estimates of oceanic anthropogenic CO_2 uptake.

(iii) Constrain turnover-times and size of land biosphere. Atmospheric $\Delta^{14}C$ is sensitive to gross exchange of CO_2 with the land biosphere. The imprint on atmospheric $\Delta^{14}C$ of these exchanges is a function of the turnover times and size of the various land carbon pools in land plants and soils and a function of recent atmospheric $\Delta^{14}C$ history. In the first few decades after the bomb tests, the land biosphere served to reduce atmospheric $\Delta^{14}C$ by absorbing a fraction of the bomb ^{14}C excess. More recently, the land biosphere has switched to being a source. Excess ^{14}C taken up by land biota in the first few decades after the bomb tests is now being given back to the atmosphere. The return of decade-old carbon from the land biota is greatest in the summer, when respiration rates are highest, so this exchange contributes to the seasonality of atmospheric $\Delta^{14}C$. Measurements of the seasonality in $\Delta^{14}C$, its spatial distribution, and its evolution over time can be used to improve our understanding of turnover times and sizes of land biosphere carbon pools, which in turn can improve our predictions of the role of land biota as a potential sink for anthropogenic CO_2.

Technical Objectives

The primary analytical objective was to analyze archived ~biweekly CO_2 samples from the SIO CO_2 network (Figure 1) which will provide a baseline of the latitudinal and temporal variability in $\Delta^{14}C$ for "clean air" sites. These data reflect what is in effect is a carbon isotope accounting of the fluxes of carbon between reservoirs (ocean, terrestrial) and 'dilution' of ^{14}C with fossil fuel derived carbon dioxide and 'enrichment' from the

stratosphere (where ^{14}C is naturally formed). Simultaneously, we participated in the Atmospheric Tracer Transport Model Intercomparison Project (TransCom) to quantify and diagnose the uncertainty in inversion calculations of the global carbon budget that result from errors in simulated atmospheric transport. The goal of the modeling was to build up the knowledge base and to utilize the $^{14}CO_2$ data in specific inversions and network design experiments.

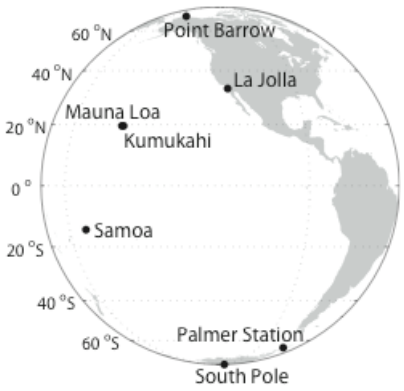

Figure 1. Location of the Scripps CO_2 sites where we have developed $\Delta^{14}C$ time-series.

The long-term trend in all of the time-series approaches -5.5‰ per year with Point Barrow exhibiting the most consistent and largest seasonal cycle (Figure 2). The larger seasonal cycle (relative to *eg*., Mauna Loa, American Samoa) is to some extent a reflection of the asymmetry of fossil fuel utilization with most of the utilization in the northern hemisphere. Atmospheric circulation brings high CO_2 air from Eurasia to the Arctic. The latitudinal gradient (Figure 3) includes a difference in the influence of ocean to atmosphere $^{14}CO_2$ exchange in the southern ocean and the influence of more fossil fuel CO_2 emissions in 2005-2007 versus 1988-1989. With regards to future measurement programs: combining atmospheric and oceanic measurements in the Southern Hemisphere will provide a means to 'monitor' and test the hypothesis that as climate warms due to anthropogenic activities that the southern ocean will become more stable (due to both warming and freshening which have an additive effect on density) and thus decrease the overturning and deep-water production in the Southern Ocean.

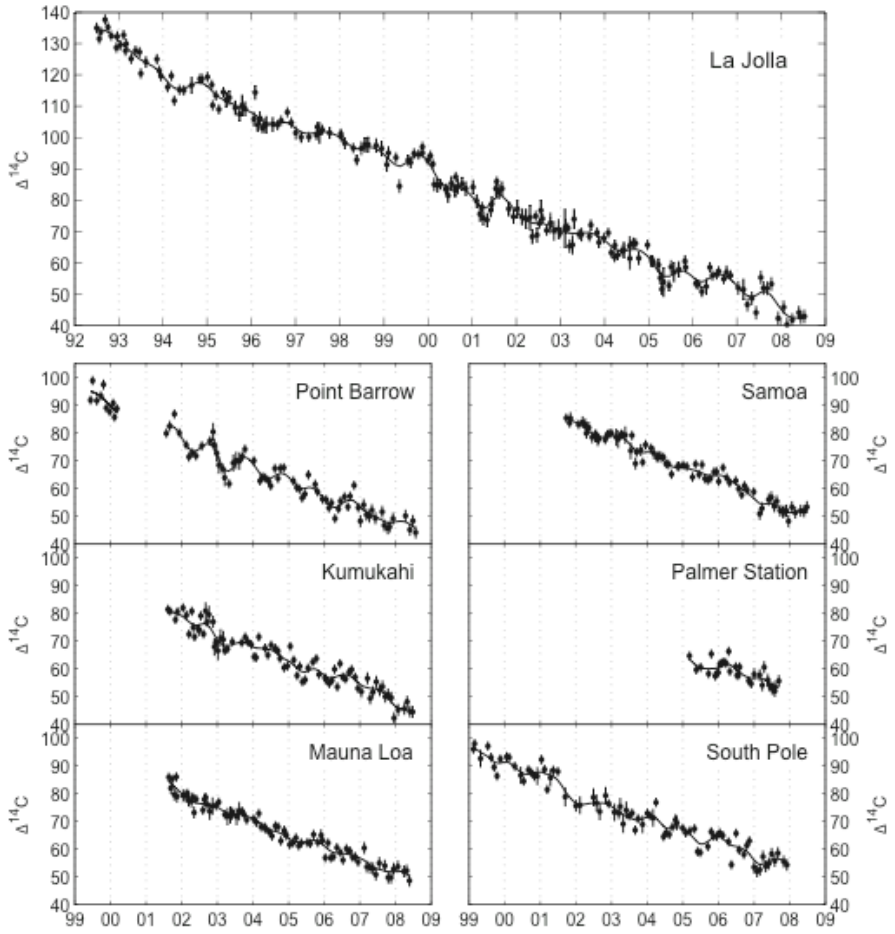

Figure 2. Composite $\Delta^{14}C$ time-series of the SIO CO_2 stations *(Graven et al., in preparation)*.

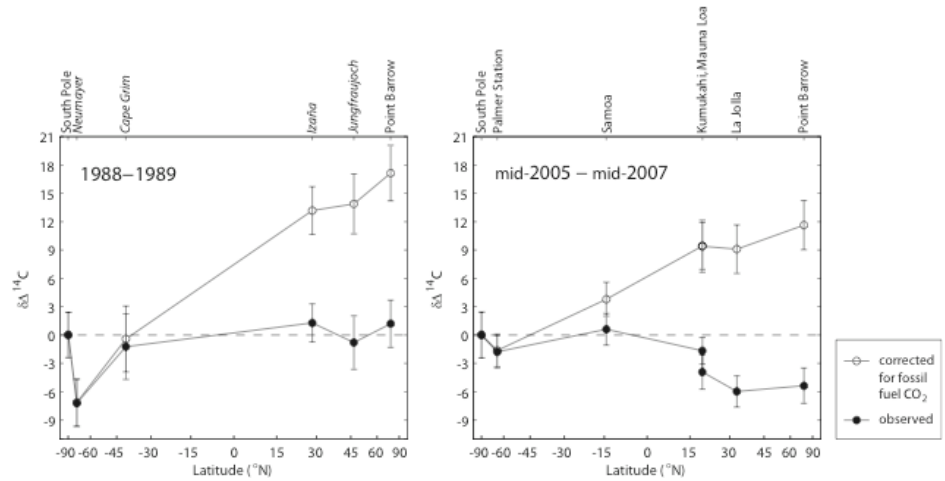

Figure 3. Example of the evolution of the latitudinal gradient between 1988-1989 and 2005-2007 relative to the South Pole (*Graven et al., in preparation)*. The effect of fossil fuel CO_2 uses the TransCom emission basis functions.

As an illustrative example of attributing the source of CO_2 in a parcel of air, we

participated in vertical (aircraft) profile and sampling in an urban (Denver, CO) and rural (Kemmerling, CO) setting. A simple endmember mixing model was then constructed to partition CO_2 deviations relative to the free-troposphere (Figure 4). The inclusion of $^{14}CO_2$ measurements allows the explicit estimation of fossil fuel CO_2 addition relative to *eg*., night time respiration or photosynthesis (CO_2 uptake by plants). The results have been recently published in Tellus (LLNL-JRNL-405950).

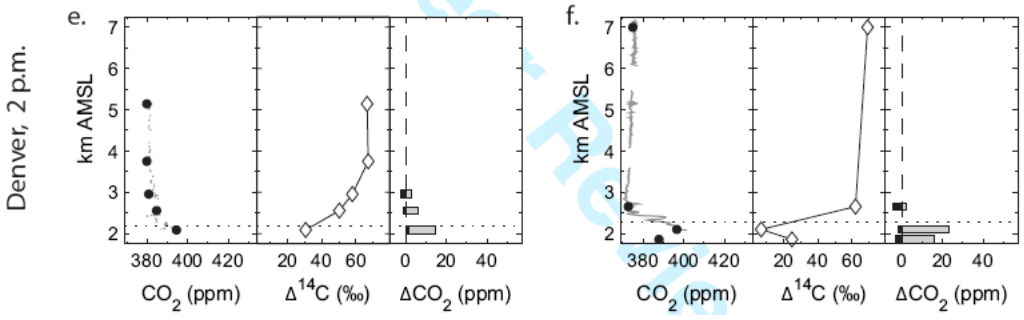

Figure 4. Early afternoon vertical profiles of CO_2 (thin grey in situ aircraft analyses, solid symbols flasks), $\Delta^{14}CO_2$, and fossil fuel CO_2 (gray bar) and biosphere (black bar) partitioning estimated from free troposphere (background) and diurnal respiration endmembers using $\Delta^{14}C$ for May 20 (e) and July 20 (f) 2004 over Denver Colorado. Dashed line is the approximate position of the boundary layer. From Graven *et al*., in press *Tellus* (2009).

Transcom style modeling utilized LLNL's "IMPACT" chemical tracer transport model and GEOS4 assimilated meteorology. The transcom protocol divides the globe into 22 regions. In addition to the standard Transcom comparisons (UCRL-JRNL-231740, UCRL-JRNL-231758**)** we took advantage of the explicit utility of $^{14}CO_2$ measurements. For utilization of the SIO $\Delta^{14}CO_2$ (and pCO_2, $\delta^{13}C$) data, we further simplified the globe to three latitude bands and six regions (Figure 5). A simplified fossil fuel proxy was developed which is directly relatable to $\Delta^{14}CO_2$. The inversion seeks to minimize the error between an a priori estimate of fossil fuel emissions (provided as a bottom boundary basis function) and that inferred from the observations (Figure 6).

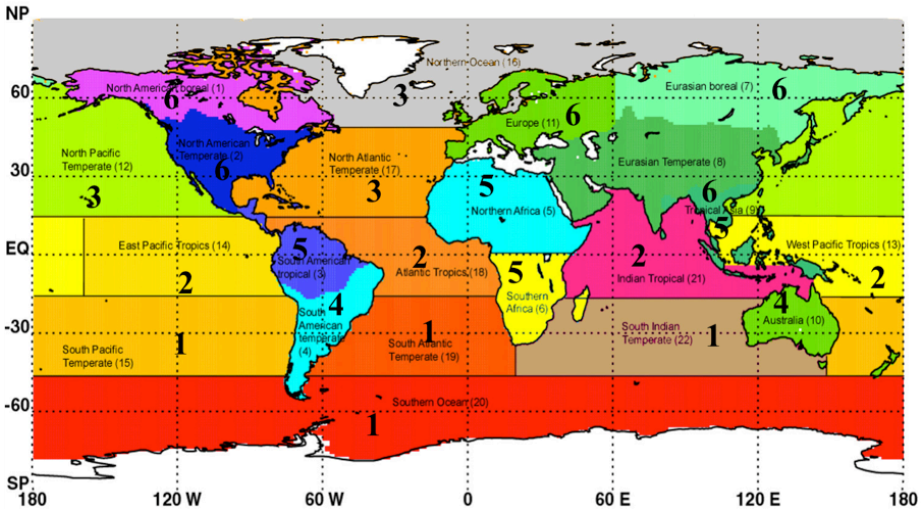

Figure 5. Simplification of the twenty two "basis" regions into three latitude bands and six regions for utilization with the SIO $^{14}CO_2$ time-series.

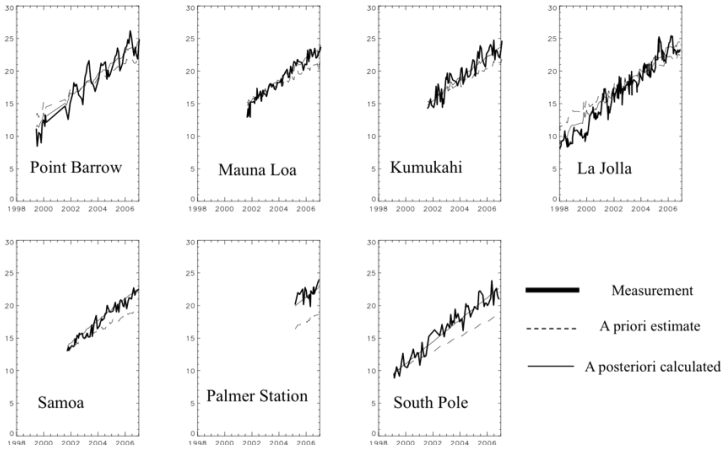

Figure 6. Comparison of the inversion solution (a posterori) with the original basis function (a priori) for the SIO $^{14}CO_2$ time-series (*Cameron-Smith et al., in preparation*).

The inversion solution using the seven SIO sites yields four (4) degrees of freedom. This can be loosely translated to mean that, using the SIO sites, there is enough information to constrain three regions and an offset. The inversion solution wants to increase the amount of "fossil fuel CO_2" emitted from the southern ocean. The inversion cannot differentiate the effect of ^{14}C-free fossil fuel CO_2 and that of low-^{14}C (relative to the atmosphere) CO_2 that outgases from the southern ocean. This means that the a priori CO_2 flux for the southern ocean is not correct.

The inversion solution to minimize the error function can also be used to assist in an observational network design. In the context of the original 22 Transcom regions, five to seven additional $^{14}CO_2$ time-series (*ie*. 12-14 in total) would allow one to constrain four additional regions (Figure 7).

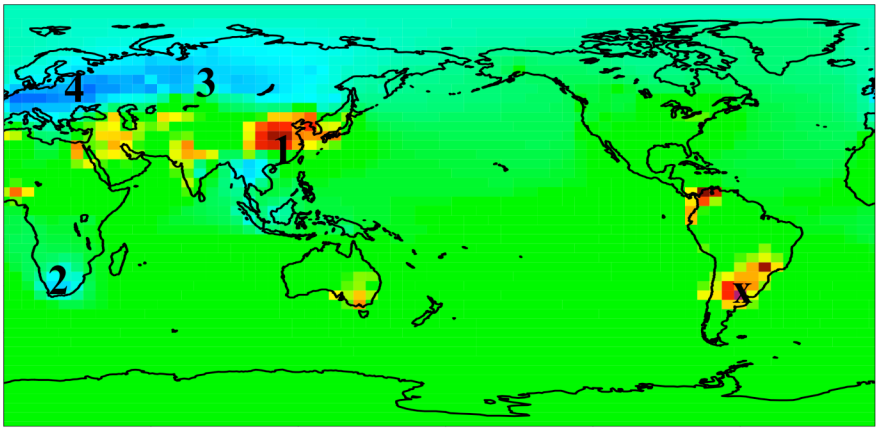

Figure 7. Optimal network results using transcom regions and basis functions to constrain fossil fuel CO_2 emissions and carbon budget. Five additional locations (in addition to the SIO network) would yield 9 degrees of freedom: 8 regions constrained and an offset.

Future Plans

In addition to our published articles (see below) several more manuscripts are in the works, the lead writing of the time-series $^{14}CO_2$ data is being pursued by Dr. Heather Graven, whose dissertation research the results are contained within. The IMPACT-Transcom network design 'experiment' is being written up by Drs. Cameron-Smith and Bergmann. The stratospheric data has provided a new model collaboration between Drs. Cameron-Smith and Bergmann with Dr. Boering that was recently funded by the University of California's Office of the President. The extant data is currently being written up with Drs. Boering and Ms. Comfort taking the lead.

Additional and future ^{14}C analyses on clean air CO_2 as well as other sites to uniquely study aspects of the carbon cycle are under development with both NOAA and DOE program managers.

Education and Outreach:

This research was utilized in the following theses:

Advancing the use of radiocarbon in studies of global and regional carbon cycling with high precision measurements of ^{14}C in CO_2 from the Scripps CO_2 Program. Heather D. Graven, PhD, 2008, University of California – San Diego.

Measurements and analysis of post-bomb era stratospheric $^{14}CO_2$: Applications to atmospheric chemistry and transport and carbon cycle dynamics. Lauren L. Comfort, MSc 2008, University of California- Berkeley.

Presentations and Publications attributable to this project:

LLNL-JRNL-405950 H.D. Graven, B.B. Stephens, T.P. Guilderson, T.L. Campos, D.S. Schimel, J.E. Campbell, and R.F. Keeling, 2009. Vertical profiles of biogenic and fossil fuel-derived CO_2 from airborne measurements of $\Delta\ ^{14}CO_2$ and CO_2 above Colorado. *Tellus B* Mar 5 2009 DOI: 10.1111/j.1600-0889.2009.00421.x.

UCRL-JRNL- 231740 Patra, P.K., R.M. Law, W. Peters, C. Roedenbeck, M. Takigawa, I. Baker, D.J. Bergmann, et al., 2008: TransCom model simulations of hourly atmospheric CO_2: Analysis of synoptic-scale variations for the period 2002-2003. *Global Biogeochemical Cycles*, 22, GB4013, doi:10.1029/2007GB003081

UCRL-JRNL-231758 Law, R.M., W. Peters, C. Rodenbeck, I. Baker, D.J. Bergmann, et al., 2008: TransCom model simulations of hourly CO_2: experimental overview and diurnal cycle results for 2002. *Global Biogeochemical Cycles*, 22, GB3009, doi:10.1029/2007GB003050.

UCRL-JRNL-225389 H.D. Graven, T.P. Guilderson, and R.F. Keeling, 2007. Methods for high precision measurements of atmospheric $^{14}CO_2$ at LLNL. *Radiocarbon*, 49, 349-356.

UCRL-ABS-234329 H.D. Graven, T.P. Guilderson, and R.F. Keeling, 2007. New Observations of Regional Variability in Delta-^{14}C of Background CO_2 from the Scripps CO_2 Program. *EOS Trans. AGU* 88(52), B51E-04.

UCRL-ABS-234372 D. Bergmann, P. Cameron-Smith, T.P. Guilderson, K. Grant, and H. Graven, 2007. Constraining regional fossil fuel CO_2 emissions and choosing an optimal measurement network using ^{14}C observations, modeling, and inversions. *EOS Trans. AGU* 88(52), B51E-03.

UCRL-PRES-234905 H.D. Graven, R.F. Keeling, T.P. Guilderson, 2007. $\Delta^{14}CO_2$ From the Scripps CO2 Program. International CO_2 Experts Meeting, 14th WMO/IAEA Meeting of Experts on Carbon Dioxide, Other Greenhouse Gases, and Related Tracer Measurement Techniques, Helsinki.

UCRL-PRES-234691 T.P. Guilderson, H.D. Graven, and R. F. Keeling, 2007. $^{14}CO_2$ Measurements in Clean Air Samples: A Record of the Carbon Cycle and Anthropogenic Influences. NOAA Office of Global Program's North American Carbon Program Meeting, Silver Spring Maryland

UCRL-ABS-225392 H. D. Graven, B. Stephens, R. F. Keeling, T. P. Guilderson, T. L. Campos, and D. S. Schimel, 2006. Identifying CO_2 Sources With Vertical Profiles of $\Delta^{14}CO_2$ Above Colorado. *EOS Trans. AGU*, 87(52) B41G-08.

UCRL-ABS-218357 H.D. Graven, T.P. Guilderson and R.F. Keeling, 2006. High-precision AMS-^{14}C measurements on atmospheric CO_2 samples at CAMS. 19th International Radiocarbon Conference, April 3-7, 2006. Oxford UK.